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Studies on the Determination of Metals by Extraction Method of Metal Organic Compound. IX

Determination of Antimony and Bismuth with Antipyrine and Potassium Iodide*

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Synopsis

Antimony and bismuth, when potassium idodide and antipyrine were added to them in acid solution, formed compounds of antipyrine-antimony iodide and antipyrine-bismuth iodide respectively which could be extracted with an organic solvent, and photometric determinations of antimony and bismuth were made by using such extracts. Both these compounds were extracted with chloroform and antimony and bismuth could be determined to the very small amount of 1 γ by measuring the absorbance of the extracts at 430~460mμ for antimony and at 345 mμ for bismuth.

I. Introduction

A method for the determination of bismuth by extraction with an organic solvent by using antipyrine and ammonium thiocyanate was reported(1). In the present study, another method was examined by using antipyrine and potassium iodide. Gotô and Suzuki(2) extracted the complex iodide of bismuth with isoamyl alcohol and measured the absorption in the ultraviolet region. West, Senise and Carlto(3) utilized bismuth iodide for spot reaction in the presence of methyl isobutyl ketone. Takagi and Nagase(4) reported the use of a compound formed by $HBiI_4$ with antipyrine and methyleneamine for the detection of bismuth. The present author carried out the determination of bismuth, basing on the fact that bismuth forms a compound of antipyrine-bismuth iodide with antipyrine and potassium, and that the compound can be extracted with an organic solvent, and measuring the absorption of this extract in the ultraviolet region. Antimony also formed a yellow precipitate with antipyrine and potassium iodide, the precipitate was extracted with an organic solvent, and the extract showed an absorption in the ultraviolet region. By the photometric measurement of this absorption, microdetermination of antimony was made.

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* The 818th report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Chemical Society of Japan, **75** (1954), 1291.

(1) E. Sudô, J. Chemi. Soc. Japan, **74** (1953), 918.
(2) H. Gotô, and S. Suzuki, Ibid., **74** (1953), 142.
(3) P.W. West, P. Senise and J.K. Carlto, Anal. Chim. Acta, **6** (1952), 488.
(4) Takagi and Nagase, J. Pharm. Soc. Japan, **56** (1936), 94.

II. Experimental results

Apparatus was Beckman model DU spectrophotometer with 1 cm cell. Reagents was as follows :

Standard antimony solution (100γ/ml) : antimony potassium tartrate was dissolved in sulfuric acid and brought to 4 N sulfuric acid; Standard bismuth solution (100γ/ml) : metallic bismuth was dissolved in a small amount of nitric acid and diluted with water; Antipyrine solution : 5 per cent aqueous solution of antipyrine J. P.; Potassium iodide solution : 10 per cent aqueous solution; Sulfuric acid, Nitric acid, hydrochloric acid (distilled) ; Organic solvents : benzene, toluene, xylene, carbon tetrachloride, chloroform, ethyl acetate, amyl acetate and isoamyl alcohol, all were of the first grade reagents.

1. Antimony

(i) Experimental procedure

The antimony solution was placed in a separatory funnel, 5 ml of 8 N sulfuric acid, 3 ml of 5 per cent antipyrine solution, and 2 ml of 10 per cent potassium iodide were added to them and mixed, and allowed to stand for 15 minutes. This was shaken with 5 ml of chloroform, the chloroform layer was separated and the optical density of the chloroform extract was measured in a 1 cm cell.

(ii) Absorbance curve

The transmittance of the extract obtained in the above was measured between 320 and 1000 mμ and absorbance curve was plotted. In this case chloroform was taken as the standard. The absorbance curves thereby obtained are shown in Fig. 1, in which curve A is that of the blank test and curve B is that containing 20γ of antimony. As seen from curve B, the absorbance increases in the ultraviolet region below 500 mμ and the maximum absorbance appears at 365 mμ. The absorbance of the blank also shows the same tendency and at 360 mμ, the absorbance of the blank is so large that it is unsuitable for the determination. Calibration curves plotted at 430, 440, 450 and 460 mμ, in which region the absorbance of the blank was comparatively small, showed that the amount of the metal and the coefficient of extinction were in linear relationship, as will be shown by the following experiments, that

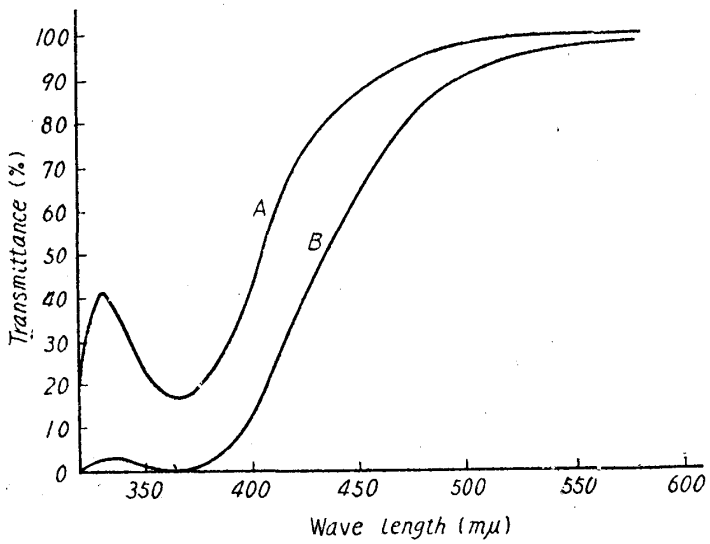

Fig. 1. Transmittance curve of antipyrine-antimony iodide complex in chloroform.
A : Blank test (chloroform as standard)
B : Antimony 20 γ (chloroform as standard)

430~460 mμ was chosen as the optimal wave length.

Fig. 2 shows the absorbance curves obtained with various amounts of antimony, being the blank as the standard. Curve A is that of 20γ antimony and curve B is that of 50 γ antimony.

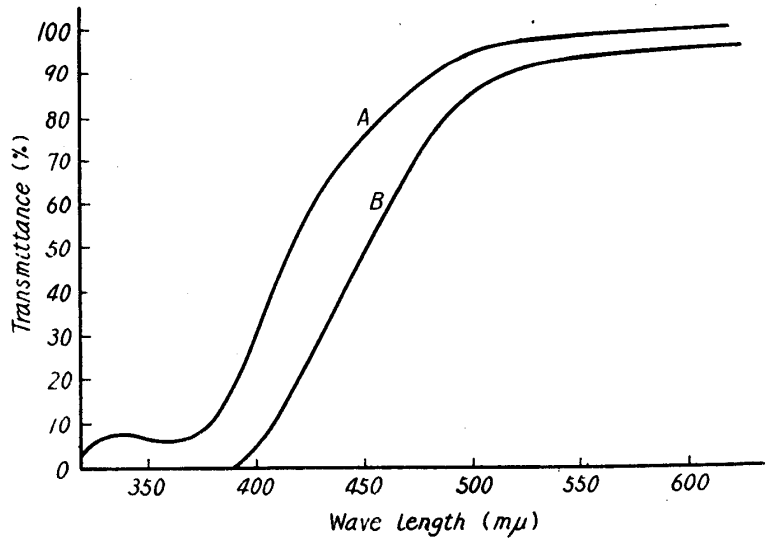

Fig. 2. Transmittance curve of antipyrine-antimony iodide complex in chloroform.
A: Antimony 20 γ (blank test as standard)
B: Antimony 50 γ (blank test as standard)

(iii) Solvents

Comparative examinations were made on the extractability of various solvents and the absorbance of the solvent measured. It was found that the extraction was best effected by isoamyl alcohol but the absorbance of the blank was very great. The extraction was not effected by benzene, toluene, xylene, and carbon tetrachloride. Chloroform was able to effect good extraction and molecular extinction coefficients at 430, 440, 450 and 460 mμ are shown in Table 1. Extraction of 30 and 60 γ of antimony with two portions of each 5 ml of chloroform showed that the absorbance in the second extract was almost negligible and that subsequent extractions were effected by one extraction with 5 ml of chloroform.

(iv) Duration of standing after addition of the reagents

Table 1.

Wave length (mμ)	Molecular extinction
430	5832
440	4663
450	3658
460	2763

The time of standing which was taken until extraction with chloroform was varied, after the addition of 3 ml of 5 per cent antipyrine solution and 2 ml of 10 per cent potassium iodide solution to the antimony solution (50 γ Sb), and the absorbance obtained from these extracts are plotted in Fig. 3. As seen from this graph, the time of standing seems to be the most suitable at 10~20 minutes. Below 10 minutes the absorbance is scattered, while above 20 minutes, although the absorbance increases, the blank values also increase and become unstable.

(v) Concentration of the acid

Suitable concentration of the acid for extraction was examined. Fig. 4 shows the results of the absorbance measured at 430 mμ. The optimal concentration of sulfuric acid is 2~5 N; hydrochloric acid 1~2.5 N; nitric acid 1.5~4.5 N.

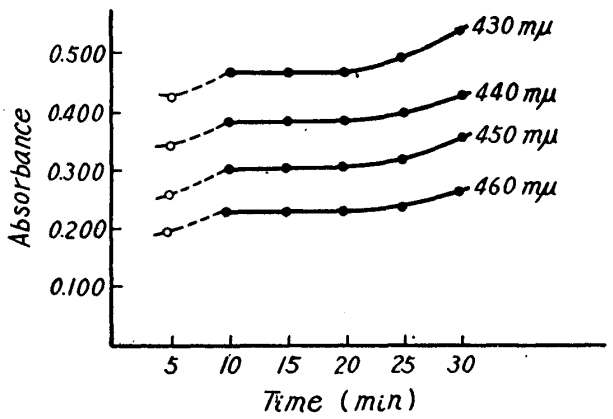

Fig. 3. Relation between absorbance and time of standing after addition of reagents.

(vi) Amount of the reagents

Extraction was made with a solution containing 50 γ of antimony in 3 N sulfuric acid, with 2 ml of 10 per cent potassium iodide and various amounts of antipyrine solution. It was thereby found that 2 ml of 5 per cent antipyrine solution was quite sufficient. Under the same conditions, with 2 ml of 5 per cent antipyrine solution and various amounts of potassium iodide, the extraction was made and optically determined, from which it was found that 2 ml of 10 per cent potassium iodide was also sufficient.

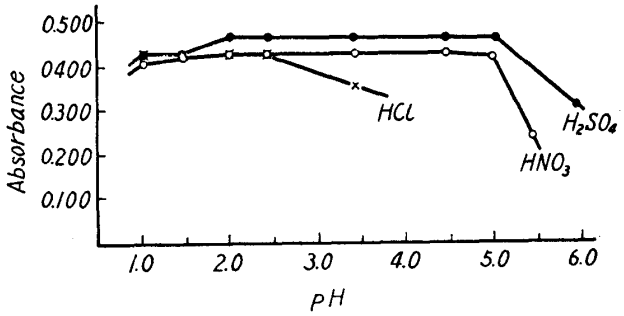

Fig. 4. Relation between absorbance and concentration of hydrogen ion

(vii) Relation between the amount of antimony and absorbance

Using 5 ml of 8 N sulfuric acid, 3 ml of 5 per cent antipyrine solution, 2 ml of 10 per cent potassium iodide solution, and varying the amount of antimony, the solution was extracted with 5 ml of chloroform after standing for 15 minutes. The absorbance of the extract was measured at 430, 440, 450 and 460 mμ. As shown in Fig. 5, a linear relationship exists and antimony is determinable in a range of 1~100 γ.

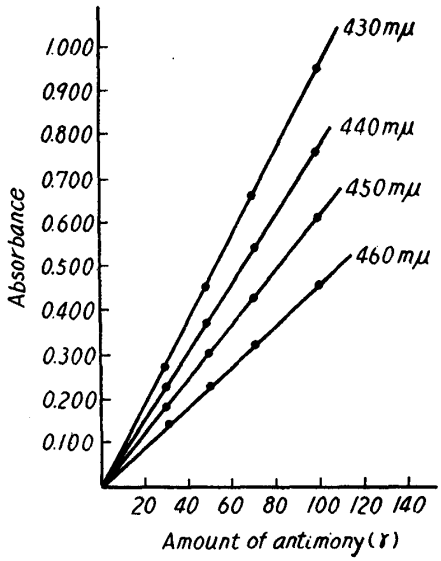

Fig. 5. Calibration curve for antimony.

(viii) Effect of divers ions

Possibility of interference by ions likely to be present was examined, and it

was found that copper, aluminium, barium, calcium, nickel, cobalt, iron, chromium silver and quinquevalent arsenic ions interfered, but not mercury, bivalent tin and trivalent arsenic.

2. Bismuth

(i) Experimental procedure

Bismuth solution was placed in a separatory funnel, 5 ml of 3 N sulfuric acid, 2 ml of 5 per cent antipyrine solution and 1 ml of 10 per cent potassium iodide were added to it, mixed and allowed to stand for 10 minutes. This mixture was shaken with 5 ml of chloroform, the chloroform layer was separated and its optical density was measured in a 1 cm cell.

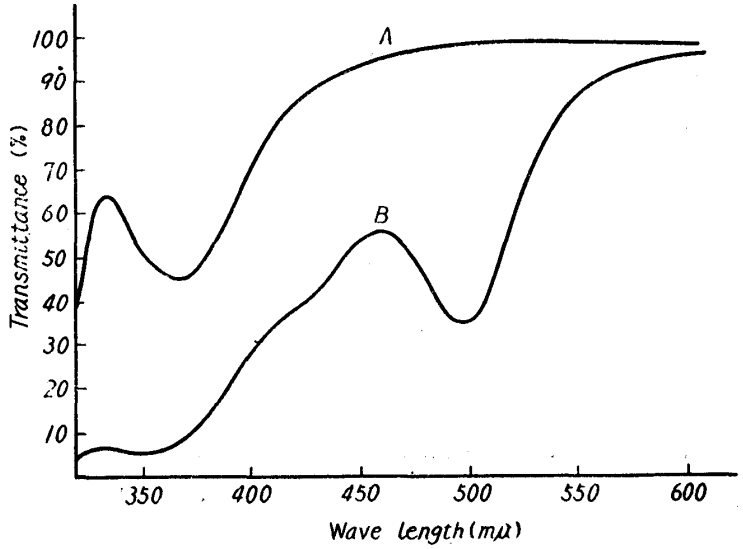

Fig. 6. Transmittance curve of antipyrine-bismuth iodide complex in chloroform.
A: Blank test (chloroform as standard)
B: Bismuth 50 γ (chloroform as standard)

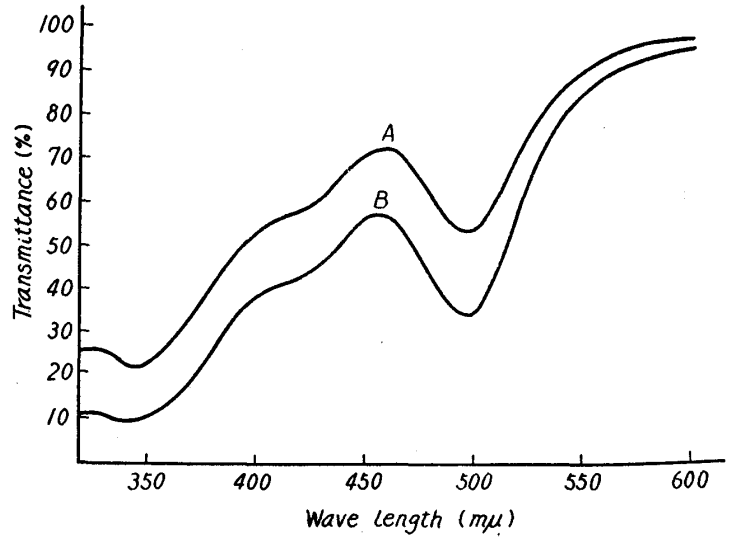

Fig. 7. Transmittance curve of antipyrine-bismuth iodide complex in chloroform.
A: Bismuth 30 γ (blank test as standard)
B: Bismuth 50 γ (blank test as standard)

(ii) Absorbance curves

Transmittance of the above extract was measured between 320 and 1000 mμ and the absorbance curves were plotted. The absorbance curves obtained with chloroform, as the standard, are shown in Fig. 6, in which curve A shows the absorbance of the blank test, and curve B that of 50 γ of bismuth. As seen from Fig. 6, there is an absorbance at 500 mμ and the maximum lies at 345 mμ. The maximum absorbance of the blank is at 370 mμ, and the absorbance becomes greater at shorter wave lengths below 320 mμ. Calibration curves plotted from the measurements at 345 and 500 mμ showed a linear relationship to exist between the amount of the metal and the absorbance, as will be apparent from the later experiments. Therefore, these wave lengths were adopted as the most suitable.

Fig. 7 shows the absorbance curves obtained with the blank as the standard and various amounts of bismuth. Curve A is the absorbance of 30 γ of bismuth and curve B that of 50 γ of bismuth.

(iii) Solvents

Comparative examination was made on the extractability of each solvent and the optical density of the extract obtained. It was found that chloroform and isoamyl alcohol could effect the extraction, but carbon tetrachloride, benzene, toluene, xylene and amyl acetate could not. With ethyl acetate and isobutyl alcohol, the absorbance of the blank was too large and unsuitable for the determination. The extract with isoamyl alcohol showed absorbance in a shorter wave length, possessing the absorbance maximum at 470 mμ and the measurement became impossible at wave lengths below 360 mμ due to the large absorbance of isoamyl alcohol itself. Molecular extinction coefficient of bismuth, by extration with chloroform, is 20900 at 345 mμ and 10032 at 500 mμ, and by extraction with isoamyl alcohol, 6150 at 470 mμ.

(iv) Duration of standing after addition of the reagents

The time of standing which was taken until extraction with chloroform was varied, after the addition of 5 ml of 3 N sulfuric acid, 2 ml of 5 per cent antipyrine solution, and 1 ml of 10 per cent potassium iodide solution to the bismuth solution (50γ Bi), and the absorbance was measured. The results showed that the time of standing was the most suitable at 8~30 minutes, the values of the blank becoming greater when allowed to stand longer, while the absorbance values came out lower with less than 5 minutes' standing.

(v) Concentration of the acid

The range of acid concentration suitable for the extraction was examined. Results of absorbance measured at 500 mμ are shown in Fig. 8, from which it is seen that the suitable reange is 0.5~1.5 N of sulfuric acid, 0.4~0.7 N of hydrochloric acid, 0.2~0.9 N of nitric acid.

(vi) Relation between the amount of bismuth and absorbance

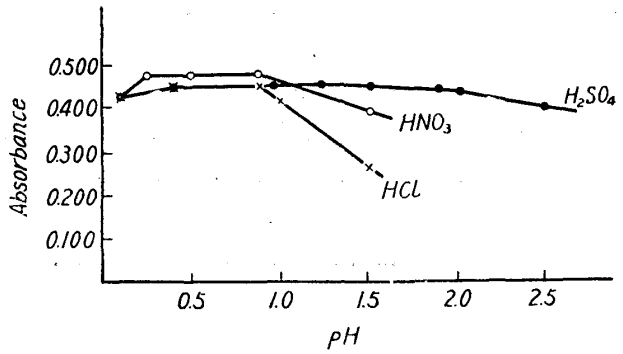

Fig 8. Relation between absorbance and concentration of hydrogen ion.

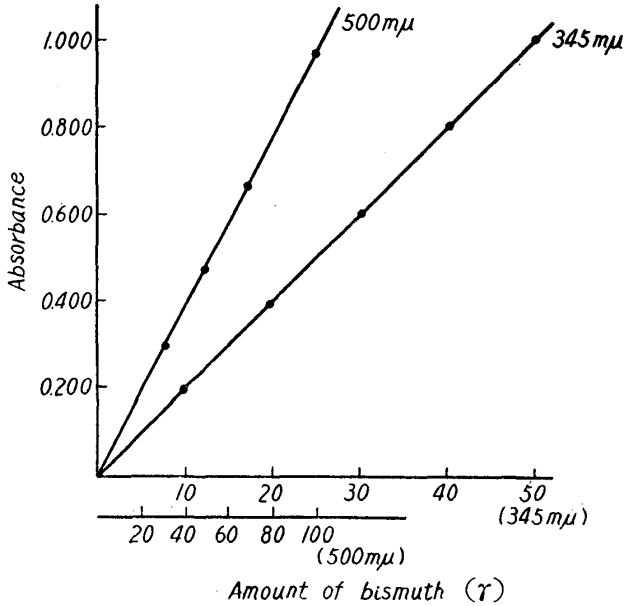

Fig. 9. Calibration curve for bismuth.

Using 5 ml of 3 N sulfuric acid, 2 ml of 5 per cent antipyrine solution, 2 ml of 10 per cent potassium iodide solution, and varying the amount of bismuth, the solution was extracted with 5 ml of chloroform, after standing 10 minutes. Fig. 9 shows the absorbance obtained at 345 and 500 mμ, showing a linear relationship to exist in both cases. Measurement at 345 mμ made it possible to detect 1γ of bismuth.

(vii) Effect of divers ions

Possibility of interference by ions usually present was examined. It was found that cobalt, nickel, trivalent arsenic, calcium, chromium and zinc did not interfere in the determination, while copper, iron, quinquevalent arsenic, cadmium and aluminium ions did interfere. The presence of 20γ of copper or iron against 50γ of bismuth interfered with the determination.

Summary

(1) Addition of potassium iodide and antipyrine to the acid solution of antimony or bismuth salt results in the formation of antipyrine-antimony or antipyrine-bismuth iodide compound which can be extracted with an organic solvent. Determination of antimony and bismuth by the photometric measurement of such extracts was studied.

(2) Antimony compound is extracted well from its acid solution with chloroform and 1~100γ of antimony can be determined photometrically at 430~460 mμ.

(3) Bismuth compound is extracted from its acid solution with chloroform, the optimal wave lengths for its photometric determination is at 345~500 mμ, and 1~50γ bismuth can be determined.

Acknowledgement

The present author takes this opportunity to extend her deep gratitude to Prof. H. Gotô for his kind guidance throughout the course of this study.